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Ab initio studies on band structure of $CaTiO_3$

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Abstract The electronic structure, energy band structure, total density of states (DOS) and electronic density in cubic crystal $CaTiO_3$ are studied using WIEN2k package. This employs the full potential – linearized augmented plan wave (FP – LAPW) method in the framework of the density functional theory (DFT) with the generalized gradient approximation (GGA). The results show an direct band gap of 2.6eV at the Γ point in the Brillouin zone. The calculated band structure and density of states of $CaTiO_3$ agree with the previous experimental and theoretical results, as do the charge distribution and the prediction of the nature of the chemical bonding. Like other perovskite ABO_3 ferroelectrics, there is a hybridization between Ti $3d$ and O $2p$, which is responsible for the tendency to ferroelectricity.

Keywords Electronic structure, $CaTiO_3$, FP-LAPW, DFT, GGA

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1. Introduction

Ferroelectric and related perovskites having chemical formula ABO_3 are the subject of extensive investigation, both because of their technical importance and because of the fundamental interest in the physics of their phase transition [1]. The ideal structure is cubic perovskite, where the A and B cations are arranged on a simple cubic lattice and the O ions lie on the face centres nearest the B cations. Thus the B cations are at the centre of O octahedra, while the A cations lie at larger twelvefold coordinated sites.

$CaTiO_3$ is one of the alkaline earth titanates like $BaTiO_3$ and $SrTiO_3$. $CaTiO_3$ transforms from orthorhombic (Pbnm) to orthorhombic (Cmcm) followed by tetragonal (I4/mcm) and cubic (Pm3m) structures with the rise of temperature from 295 to 1600K [2]. However, there exists a controversy regarding the cubic symmetry of $CaTiO_3$ at high temperatures. Sasaki *et al* [3] have reported that the crystal structure of $CaTiO_3$ is distorted from the ideal cubic perovskite structure at high temperature. The electronic structure of $CaTiO_3$ has been the subject of many investigations [3, 5]. Most of the studies that have been carried out on the electronic structure are experimental and only a few of them are theoretical [2-6].

In 1839, Rose, a Russian mineralogist, discovered a new mineral $CaTiO_3$, which he baptized as perovskite after the name of then Russian Minister of Lands, L A Perovsky. $CaTiO_3$ is widely used in electronic ceramic materials; it is also a key component of Synroc, a synthetic rock form used to immobilize nuclear waste [7]. There has been considerable interest in the structure and phase transitions of this typical perovskite oxide.

Lemanov *et al* [8] measured the dielectric properties of $CaTiO_3$ at low temperature, and classified it as an incipient ferroelectric or a quantum paraelectric. $CaTiO_3$ is called [9, 10] a higher quantum paraelectric because its dielectric constant saturates at a higher temperature than that for other quantum paraelectrics such as $SrTiO_3$ and $KTaO_3$. Nakamura *et al* [10] compared the dielectric properties of some perovskite titanates. They pointed out that in heavier titanates, such as $PbTiO_3$ and $BaTiO_3$, the Last and Slater soft modes coexist, while in the lighter titanates, $CaTiO_3$ and $SrTiO_3$, tilts or deformation of oxygen octahedra occur at certain higher temperatures than that at which softening of the Slater or Last mode can occur. The tilts or deformation of the oxygen octahedra change the reduced masses and force constants of soft modes for ferroelectricity, harden the modes, and result in a quantum paraelectricity.

In the present study, the electronic structure, density of state and electronic density of state of perovskite $CaTiO_3$ in the paraelectric phase are calculated by the FP – LAPW method with the DFT in GGA in [11-14]. The calculated results are compared with the experimental measurements, the results are in good agreement with the experimental results.

2. The method of calculation

The calculations presented in this work were performed within the GGA to density functional theory, using the FP-LAPW method. In this method, no shape approximation on either potential or the electronic charge density is made. We use the WIEN2k [15] implementation of the method. In the cubic phase, the lattice parameters we used are a = 7.37a.u., taken from the experimental results of Kennedy *et al* [2]. The calculations have been performed considering the origin of the cell to be at the Ti site, Ca at the body-center (0.5, 0.5, 0.5) a and the three O atoms at the three face centres (0.5, 0.0, 0.0) a, (0.0, 0.0, 0.5)a and (0.0, 0.5, 0.0)a. In this calculation, the convergence parameter Rk_{max} = 7 was chosen and the others parameters are : G_{max} = 14, R_{MT} (Ca) = 2.2a.u, R_{MT} (O) = 1.75 and R_{MT} (Ti) = 1.85 a.u.I used 7 × 7 × 7 meshes which represent 20 k-points in the first Brillouin zone. Figure 1(a) shows the unit cell and Figure 1(b) the Brillouin zone of $CaTiO_3$ for this structure.

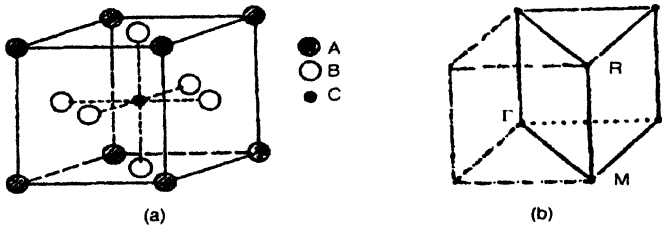


Figure 1. (a) The cubic unit cell of $CaTiO_3$ (b) The Brillouin zone for the cubic $CaTiO_3$

3. Results and discussion

3.1 Electronic structure and band structure :

The calculated energy-band structure for cubic phases $CaTiO_3$ in the high symmetry directions in the Brillouin zone is shown in Figure 2. In this method, the number 400 k-point were used and convergence parameter, Rk_{max} = 7 was chosen and the convergence is stabilized in term of energy.

The zero of the energy was set at the top of the valence. The energy scale is in eV, and the origin of energy was arbitrarily set to be at the maximum valence band. The results indicate that there is a large dispersion of the bands. Nine valence bands near Fermi level between 0.0 eV and – 5.0 eV are derived from O2p orbitals. Nine valence bands are derived from oxygen 2p orbital which are separated by a direct gap of 2.6 eV (at the Γ point) from the transition-metal d-derived (Ti) conduction band. This gap is somewhat lower than the experimental band gap 3.5eV for $CaTiO_3$ [16]. The origin of this discrepancy may be the GGA. The nine valence bands at the Γ point are the three triply degenerate levels (Γ_{15}, Γ_{25} and Γ_{15}) separated by energies of

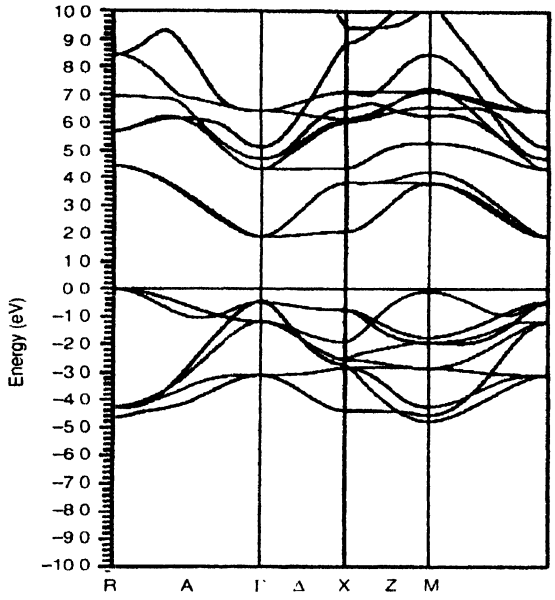


Figure 2. The calculated electronic band structure for cubic $CaTiO_3$. The zero of the energy was set at top of the valence band

0.9eV ($\Gamma_{25} - \Gamma_{15}$) and 2.2eV ($\Gamma_{15} - \Gamma_{25}$). The crystal field and the electrostatic interaction between oxygen 2p orbital produce these splitting. In the conduction band, the triply ($\Gamma_{25'}$) and doubly (Γ_{12}) degenerate levels represent t_{2g} and e_g states of titanate 3d orbital separated by energy of 2.4eV. A comparison between this result with that of Ref. [17] on $CaTiO_3$ shows almost no discernible difference except that they have obtained a direct band gap of 1.5 eV at the Γ point using the TB-LMTO and first principles ultra-soft-pseudopotential method. The calculated valence bands below the Fermi energy agree well with other

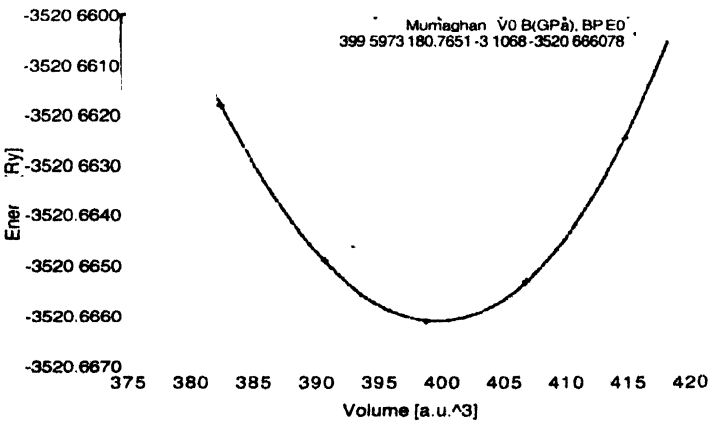


Figure 3. Total energy as a function of the volume for cubic $CaTiO_3$.

first-principle studies [17]. Electronic structure shown in Figure 2 was calculated by using the lattice constant 7.37a.u. The bulk modulus, as in *ab initio* calculations, can be obtained from the calculations of the total energy as a function of the uniform volume expansion for the cubic phase. The model calculations yield a lattice parameter of 7.365 a.u. for the static cubic structure. The bulk modulus evaluated at this equilibrium volume is 180.8 GPA, which agrees fairly well with the LDA value of 195 Gpa [18] and agrees with experimental 173 Gpa [2]. The detailed behaviour of the energy as a function of the cubic volume is shown in Figure 3, where the models results are compared with LDA calculations.

3.2 Density of states :

The electron distribution in an energy spectrum is described by the density of states (DOS) and can be measured in

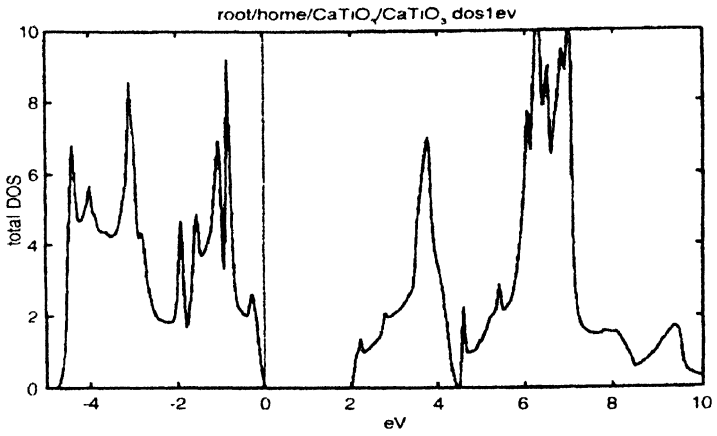
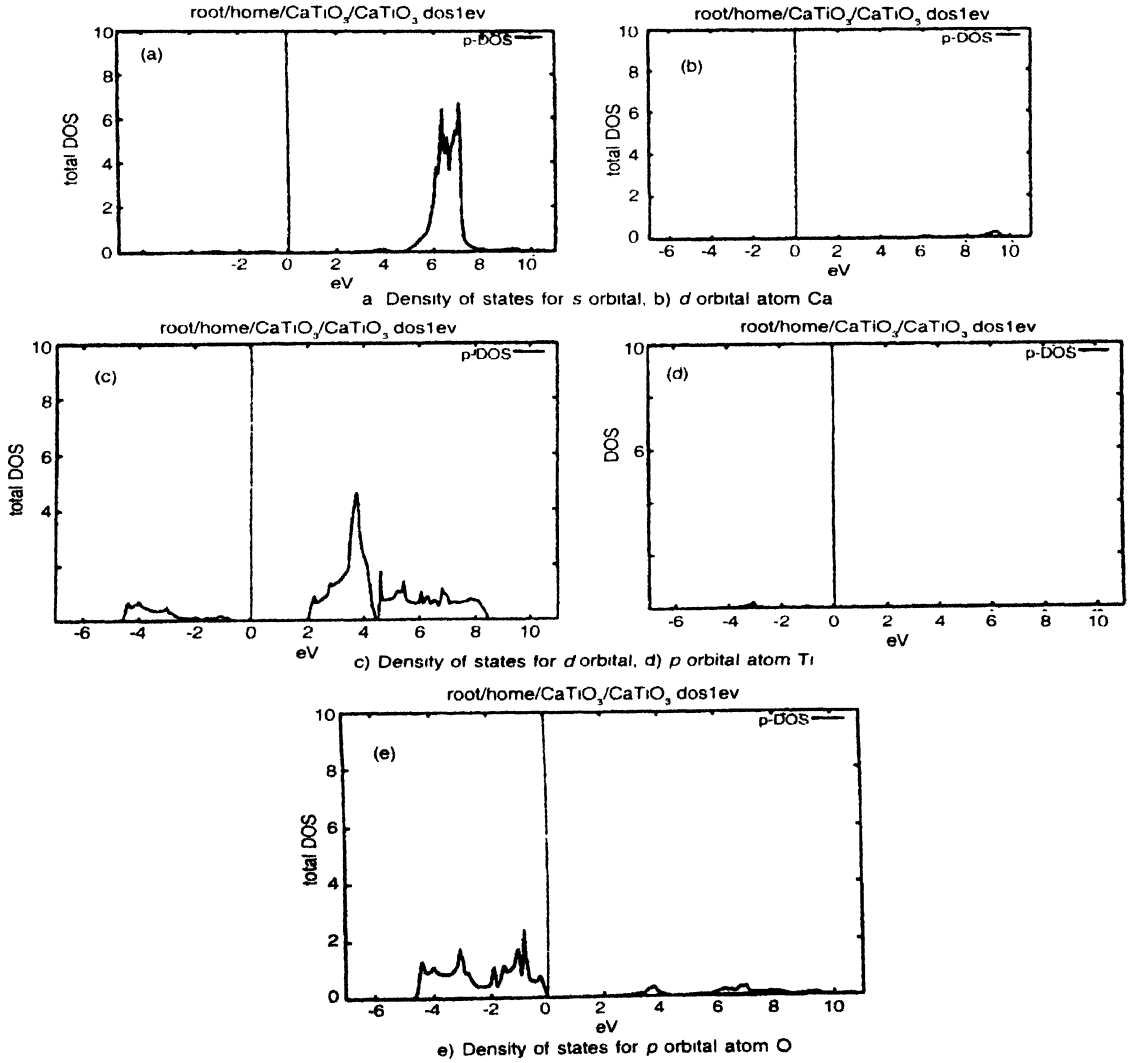


Figure 4. The density of states (DOS) for paraelectric cubic $CaTiO_3$.



a Density of states for *s* orbital, b) *d* orbital atom Ca

c) Density of states for *d* orbital, d) *p* orbital atom Ti

e) Density of states for *p* orbital atom O

Figure 5. The partial densities of states (PDOS) showing the contributions of Ca, Ti and O atoms One Ba, one Ti and three O atoms from one unit cell of cubic $CaTiO_3$ are included in the calculation.

photoemission experiments. The total DOS spectrum of cubic $CaTiO_3$ is shown in Figure 4. The valence and conduction band edges near the Fermi energy are quite sharp. In Figure 4, the zero of the energy scale shows the position of the Fermi level. The Ti 3*d* contribution is zero at the maximum of valence band but rises strongly with increasing binding energy. Conversely, the oxygen 2*p* contribution rises from zero at the minimum of conduction band with increasing energy, in which these reflect the Ti-3*d*-O2*p* covalency.

The partial density of states (PDOS) of the Ca, Ti, and O atoms are shown in Figure 5. Here, the low-energy peak around –4 to –1 eV is a contribution mainly from the O2*p* states with a small component from Ti *p* and Ti *d* orbitals. The contribution is mainly from the O2*p* state with a small component 3*d* Ti orbitals in the conduction bands edge. The valence states from –4.7eV up to the Fermi energy are dominated by O2*p* states and strongly hybridized with Ti 3*d* state. It should be pointed out that the PDOS spectrum in Figure 5 includes one Ca, on Ti atom, and three O atoms. Therefore, the height of the O2*p* DOS peak is much higher than that of the Ti 3*d* states.

3.3 Electronic charge density :

To have a clear picture about the nature of chemical bonding between the constituents of $CaTiO_3$, the distributions of charge density in two different planes have been shown in Figures 6 and 7. Figures 7 shows a sharing of charge between Ti and O due to Ti 3*d* and O2*p* hybridization. The spherical distribution of charge around Ca site as shown in Figure 6, indicates that the bonding between Ca with TiO_2 is mainly ionic. It is to be mentioned that if the self-consistently calculated valence charges has been considered within different atomic spheres, the chemical formula for the system may be written as $Ca^{+1.98}Ti^{+2.03}O_3^{1.7}$ Thus, a significant deviation has been found from the charge distribution of a prototypical ionic crystal $A^{+2}B^{+4}O_3^{-2}$. Due to the strong hybridization between O2*p* and Ti 3*d* states, there is a large amount of valence charge transfer back to Ti, revealing that the static ionic charge is significantly less than +4 and the O ion is more or less neutral, rather than charged by –2.

A quick estimate suggests that there is only a very weak hybridization of the Ca *p* state with the O2*p* state, but there is a

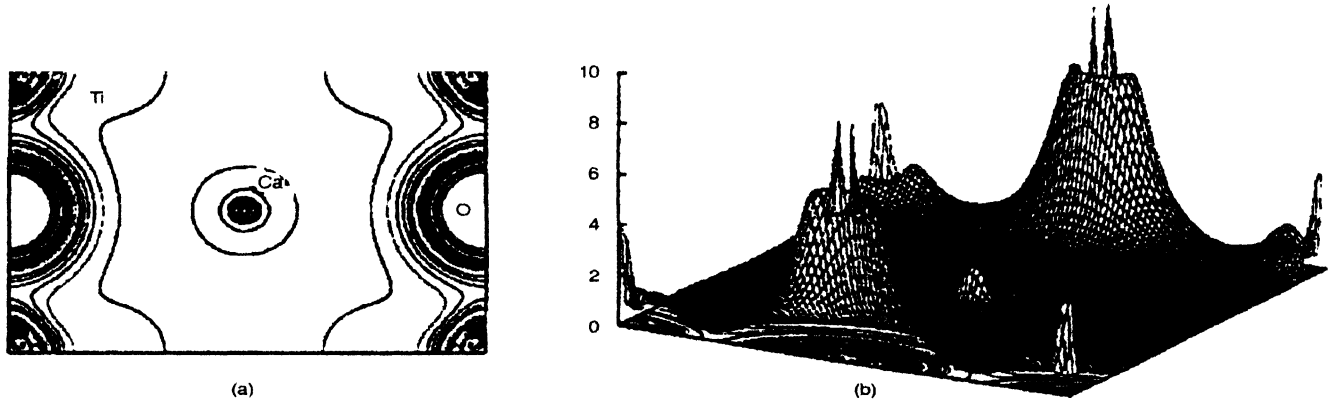


Figure 6. Electron density distribution for $CaTiO_3$ (a) in the (110) plane and (b) in three dimension

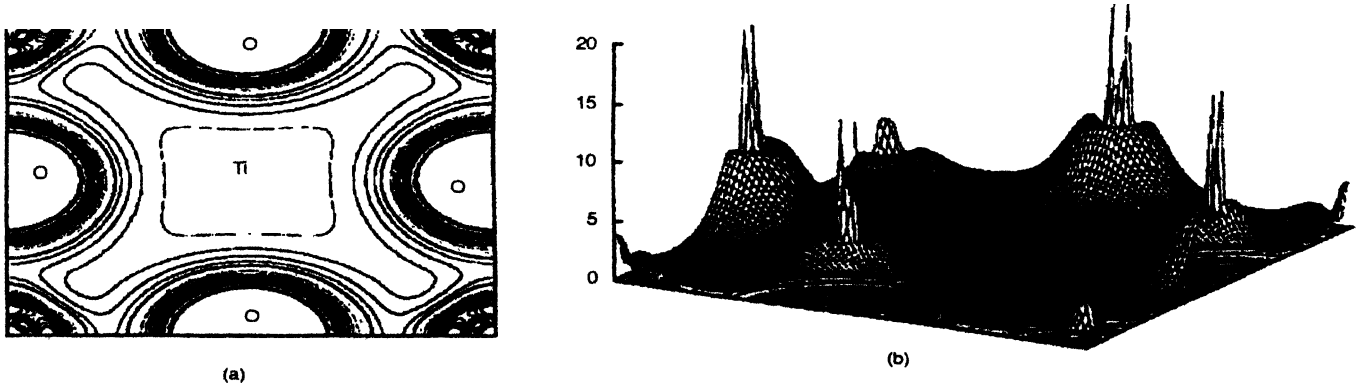


Figure 7. Electron density distribution for $CaTiO_3$ (a) in the (100) plane and (b) in three dimension.

very strong hybridization between Ti $3p$ and O$2p$ state in the valence band. This means that this system is not quite an ionic bond but it has rather a large covalency. This is shown in Figure 7 for (100) plane and in Figure 6 for (110) plane. The electron density distribution indicated that the bond between Ba and TiO_2 is ionic while that between the Ti and O is covalent.

4. Conclusion

A detailed investigation of the electronic structure and DOS of paraelectric $CaTiO_3$ in the cubic phase has been made using the FP-LAPW method. The calculations show that the fundamental gap of $CaTiO_3$ is direct at the Γ point. The calculated fundamental gap of 2.6 eV is very close to the experimentally reported value 3.5eV. The origin of this discrepancy may be GGA. The total DOS obtained from this method of calculation is compared with the experimental results. Various experiments observed that the top of the valence band is mainly composed of the O$2p$ orbitals in non-bonding states and the lower part of the valence band is formed by bonding states between Ti $3d$ and O$2p$ orbitals. The conduction band mainly consists of $3d$ states of Ti and $3d$ state of Ca. The chemical bonding of $CaTiO_3$ is also analyzed. It has been found that TiO2 complex is bonded covalently while Ca and TiO2 constituents are bonded mainly ionically.

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